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POLLUTION OF WATER AND SEDIMENTS FROM TABANOVSKA RIVER WITH HEAVY METALS FROM THE ABANDONED MINE LOJANE

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Abstract. The abandoned Lojane Mine Site and associated processing facilities are located north of city of Kumanovo on the territory of Lipkovo municipality.

The old Lojane Mine Site is located between the villages Lojane, Vaksince in area called Rudnicka Kolonija (Mine colony). The total mine site area is about 10 km^2. The exploration area includes the territory between the village Chivluk where the old smelter is located, i.e. the flotation tailings from the Lojane Mine, along the flow of Tabanovska river to the village of Gorno Konjare.

In Lojane abandoned mine, huge amount of mining waste was left without any adjustment and remediation, leading to mass erosion and transport of waste over large distance in the watershed. Chemical analysis of this waste showed high contamination by toxic heavy metals, while the leachate of waste leads to the river sediments and waters contamination.

Kew words: chemical analysis, sediments, waters, heavy metals.

ЗАГАДУВАЊЕ НА ВОДИТЕ И СЕДИМЕНТИТЕ ОД ТАБАНОВСКА РЕКА СО ТЕШКИ МЕТАЛИ ОД ПОРАНЕШНИОТ РУДНИК „ЛОЈАНЕ“

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Апстракт. Напуштената локација за рудникот „Лојане“ и придружните преработувачки капацитети се наоѓаат северно од градот Куманово на територијата на општина Липково.

Старата рудничка локација Лојане се наоѓа помеѓу селата Лојане, Ваксинце во областа наречена Рудничка колонија (Рудничка колонија). Вкупната површина на рудникот е околу 10 км^2. Испитуваниот простор се наоѓа на територијата над селото Чивлук, каде што се наоѓа старата топилница, односно флотациската јаловина од рудниот „Лојане“, па по течението на Табановска река до селото Горно Коњаре.

Во напуштениот рудник „Лојане“, огромна количина на руднички отпад останала без никаква санација и рекултивација, што доведува до масовна ерозија и транспорт на рудничкиот отпад на големи растојанија во сливот. Хемиската анализа на овој отпад покажа големо загадување со токсични тешки метали, исцедувањето на отпадот води до загадување на речните седименти и води.

Клучни зборови: хемиска анализа, седименти, води, тешки метали.

1. Introduction

The abandoned Lojane Mine (Cr and Sb) is located north of Kumanovo, near the border with Serbia. This mine was active in the period 1923 till 1979 when antimony, chromium and arsenic were extracted.

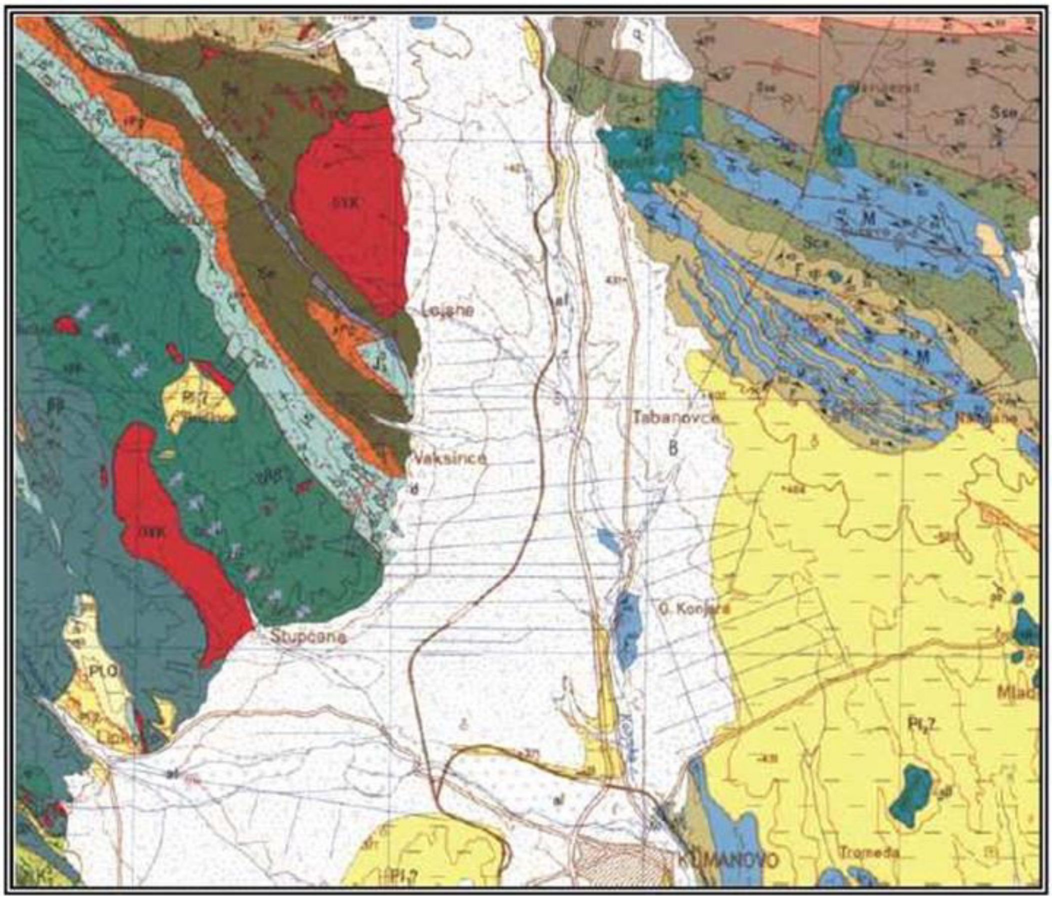
After the cessation of mining activities in 1979, complete infrastructure i.e. production facilities (underground workings), beneficiation (flotation and smelting -ore frying) facilities, ore waste dump and tailings ponds, as much as storage yards, silos and workshops were abandoned without undertaking any conservation activities. The old adits, dumps, roads and ruined objects become very dangerous sources of contamination with heavy and toxic metals (arsenic As, mercury Hg, chromium Cr^{6+} and antimony Sb) (Fig. 1). [2]

Fig. 1. Mine structures and processing facilities – tailings dump

The exposition of the mining waste to the meteoric agents, lead to release and dispersion of heavy metals in ecosystems (water, sediments and soil) over large distance. The chemical study of stream sediments, soils and waters had been conducted to estimate the degree of their contamination by heavy metals.

2. Geological settings

The area under investigations consists of a complex of Precambrian rocks, of Paleozoic metamorphic rocks and magmatites, a complex of Mesozoic sediments and magmatites, a complex of Tertiary sediments and volcanics as well as Quaternary layers and volcanics (Fig.2). [5]



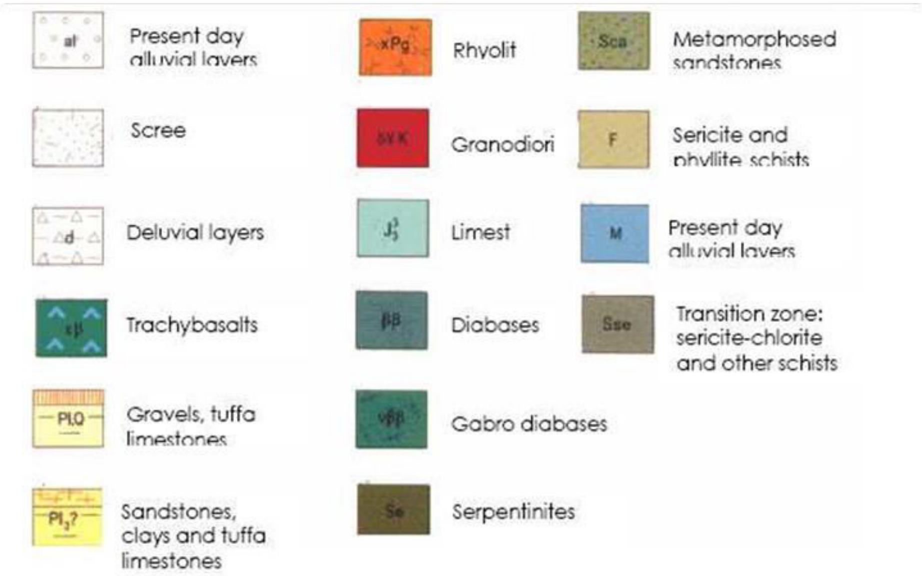


Fig. 2. Geological map of Lojane Mine vicinity [5]

Ore occurrences in the area consist of antimony and arsenic deposits. Antimony has been found in two localities – Nikustak and Lojane. At Nikustak antimony occurs in Paleozoic schists as monomineralization along the vein type. In the Lojane Mine both antimony and arsenic have been found in the serpentinite which is in contact with rhyolites. Ore bodies are complex ore veins. Major ore minerals are antimony and realgar of 6.5% As and 4% Sb.
Also, nickel, mercury and chromite have been found in this locality, but their percent is of no importance.

3. Materials and methods

3.1. Sampling

The samples of running water, sediments and soils from the surrounding fields near the Tabanovska River were taken for chemical analysis.

The fig. 3 indicate the locations where the samples were taken. Flow and drinking water samples are filled into clean, 2-liter plastic bottles bearing the appropriate water label. The water is then filtered through a 45 μm filter. For cation analysis, the water is acidified to 0.1 mol l^{-1} with pure nitric acid to minimize the deposition of dissolved material on the vessel walls.

The sediment samples were taken from the riverbed, in the part of calm and slow flow of the river, with a plastic shovel, and were filled in clean, plastic bags marked with an appropriate sediment label.

Soil samples were taken in the same way as sediments. [3]

3.2. Analytical techniques

Water samples – The taken waters have been filtered and canned with HNO_3. Each sample is taken in a plastic bottle of about 1 l. Redistilled water, nitric acid $c(HNO_3) = 15.8$ mol/l and $\rho = 1.42$ g/mol have been used as reagents.

Sediment samples - To obtain the most reliable results, the preparation of sediment samples should be performed with extreme caution. The taken samples have been dried at 80º C. Drying of sediment samples is in order to eliminate water. The dry samples have been sieved through a sieve < 63 μm.

Separate 1 g of the test sample on an analytical balance with an accuracy of 0.0001, then place in a Teflon dish and 2 cm^2 of concentrated HNO_3 to the dish have been added. The sample here is heated at 90° C for about 20 minutes to wet salts. To the residue was added 10 cm^3 of concentrated HF-acid, 2 cm^3 of HNO_3 and 3 cm^3 of concentrated $HClO_4$. The contents of the dish are left to react overnight. The next day the sample is heated to 90° C until white thick $HClO_4$ vapors and wet salts are formed. Add 5 cm^3 of HNO_3 to the wet residue and heat the contents of the dish until a clear solution is obtained, then transfer to a 100 cm^3 flask and fill up to volume with redistilled water.

Standard solutions are prepared from a basic standard solution with a concentration of 1000 mg/dm^3.

The same goes for soil tests.

Measurement – After preparation, the sample is analyzed with ICP-AES method (Inductively coupled plasma atomic emission spectroscopy). It determines the elements (macro, trace), and as a tool for final measurement of analytical signals is used Liberty 110 Inductively Cupled Plasma Atomic Emission Spectrometer in combination with a glass-concentric sprayer. [1]

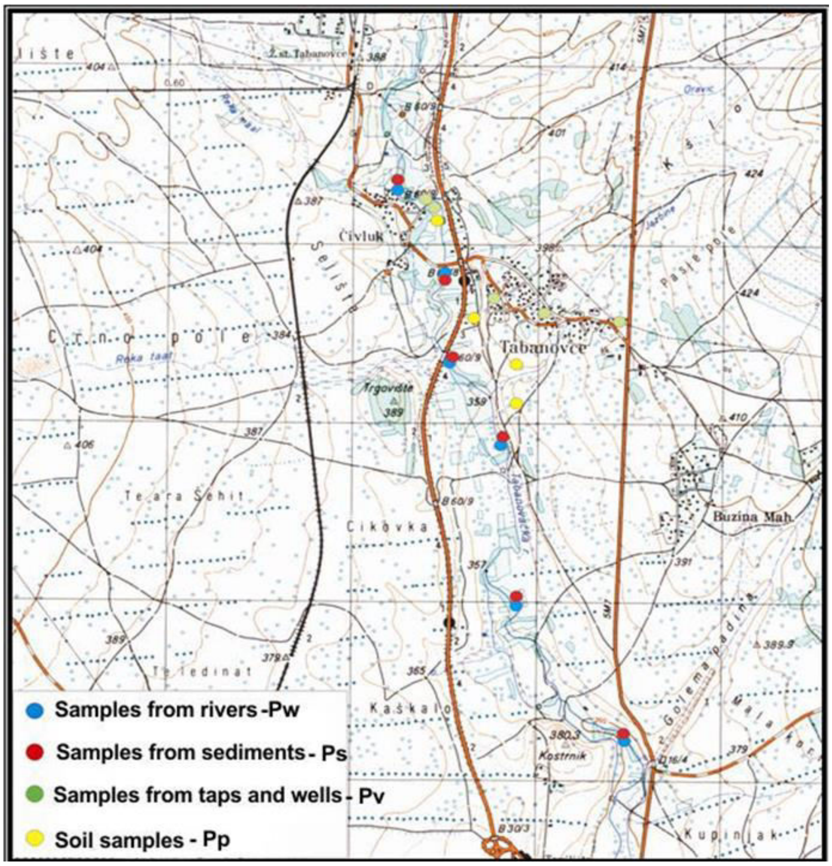


Fig. 3. Map of locations of taken samples

4. Results

4.1. Analyses of water

As part of the field activities, samples of running water (Tabanovska Reka), fountains and wells were taken which is the purpose of this paper. Flow samples were taken from places with slower water flow and collected in plastic bottles. The samples are immediately taken to a chemical laboratory and subjected to chemical analysis to determine the concentrations of heavy and toxic metals in them.The results of the performed analysis of the flow water samples are given in tab. 1, and for comparison, in the table is given maximum allowed concentrations (MAC) of heavy and toxic metals in running water and drinking water.

Table 1. Concentration (ppm) of heavy metals in the waters near Lojane

Sample	As	Cd	Cr	Cu	Pb	Zn
Pw1	0.1434	0.0036	0.0084	<0.005	0.0122	0.0382
Pw2	0.0969	0.0043	<0.005	<0.005	<0.005	0.0039
Pw3	0.0364	0.0039	<0.005	0.0100	<0.005	0.0016
Pw4	0.0442	0.0029	0.0085	0.0139	<0.005	0.1264
Pw5	0.1119	0.0042	0.0157	<0.005	0.0150	0.0000
Pw6	0.1454	0.0029	<0.005	0.0056	<0.005	0.0183
Pv1	0.0504	0.0044	<0.005	<0.005	<0.005	0.0587
Pv2	0.0229	0.0037	<0.005	<0.005	<0.005	0.0638
Pv3	0.1242	0.0031	<0.005	<0.005	0.0120	0.0538
Pv4	0.0629	0.0031	<0.005	0.0051	0.0053	0.0528
Pv5	0.0418	0.0040	<0.005	0.0202	0.0201	0.0904
MAC (Watercourses)	0.05	0.005	0.1	0.1	0.05	0.2
MAC (drinking water)	0.033	0.0015	0.004	0.002	0.015	0.0009

For all heavy metals were created diagrams on which is seen comparison of concentration and MAC of certain element.

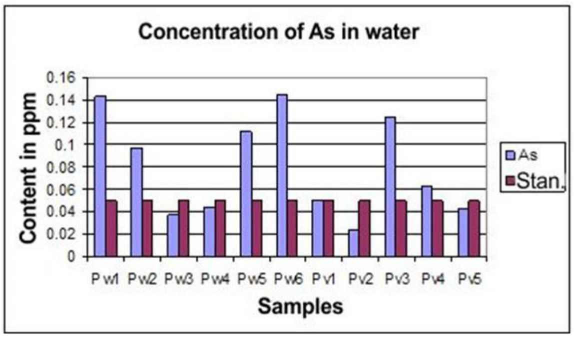


Fig. 4. Diagram of As concentration in samples of water compared with MAC

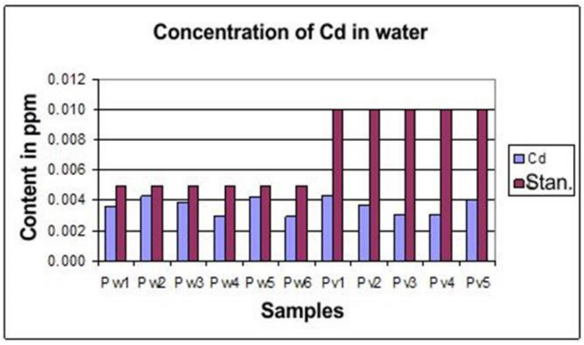


Fig. 5. Diagram of Cd concentration in samples of water compared with MAC

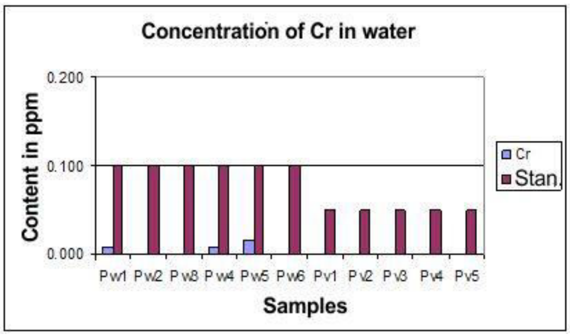


Fig. 6. Diagram of Cr concentration in samples of water compared with MAC

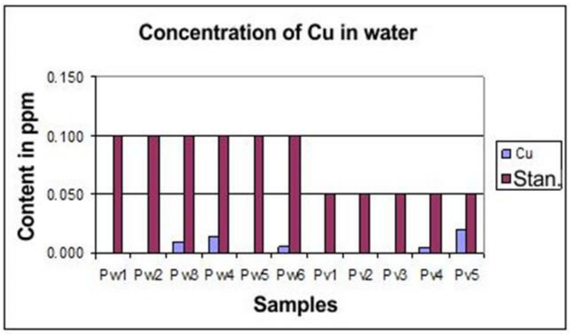


Fig. 7. Diagram of Cu concentration in samples of water compared with MAC

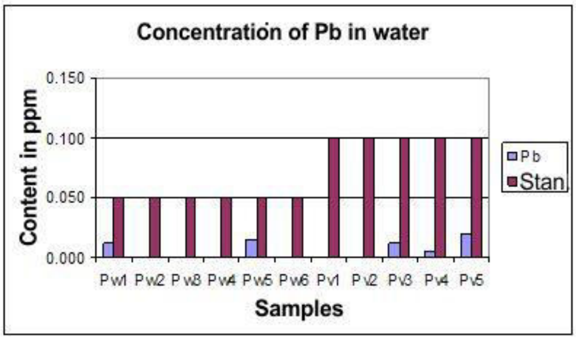


Fig. 8. Diagram of Pb concentration in samples of water compared with MAC

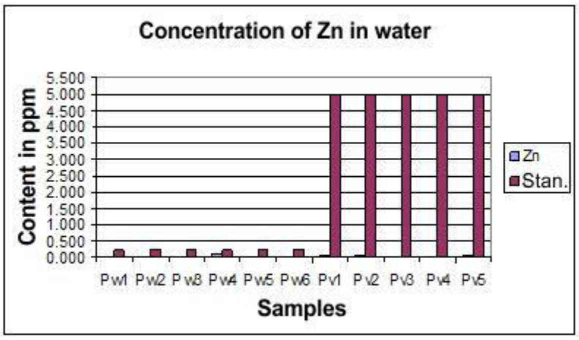


Fig. 9. Diagram of Zn concentration in samples of water compared with MAC

By studying and interpreting the diagrams shown above it can concluded that in general there is no increased concentration of heavy metals along the Tabanovska River, i.e. the area from the village Chivluk to the village Gorno Konjare, as well as in the drinking water from the fountains and wells in both villages.

The Zn concentration diagram (Fig. 9) shows that the values in all samples are much lower than the maximal allowed concentrations (MAC).

From the results for Cr (Fig. 6) it can be seen that here too the concentration is much lower than the MAC, in some samples it is not even seen on the diagram.

The As concentration in most of the samples shows high concentrations relative to the MAC. In six of the eleven taken samples, this element exceeds the prescribed standards (MAC) which can be seen from the diagram in fig. 4. In samples Pw1, Pw2, Pw5, Pw6 and Pv3 the As concentration more than doubles the permissible norms. The maximum allowed concentration of As in both running water and drinking water is 0.05 mg/l, and the highest measured concentration is 0.1454 mg/l.

From the results of the Pb concentration diagram (Fig. 8), it can be seen that its concentration is much lower than the MAC for lead in running water and drinking water.

From the diagram of the Cu concentration (Fig. 7) it can be concluded that in all samples taken from the running water and the drinking water Cu concentration is much lower than the MAC.

Cd in all samples taken is below the MAC (Fig. 2). Approximately the same Cd concentration is observed in both Tabanovska River and drinking water. The maximum allowed concentration of Cd in running water is 0.005 mg/l, and in drinking water is 0.01 mg/l.

4.2. Analyses of river sediments

The river sediments samples are taken from the peripheral parts of the riverbed, where the flow is quiet and slow. Results from analyses are given in table 2.

Table 2: Concentration of metals in the sediments of the Tabanovska river [4]

Element	Ps1	Ps2	Ps3	Ps4	Ps5	Ps6	NOAA
Zn (ppm)	160,344	111,809	79,2652	117,863	80,2880	76,3559	98
Cr (ppm)	67,2979	66,4599	95,304	72,4886	151,601	123,269	36.29
Cu (ppm)	54,4664	40,7060	35,0523	48,9168	34,3243	37,0419	28.01
Pb (ppm)	42,8056	27,5608	27,5511	26,3628	26,3908	23,3983	37
Cd (ppm)	5,8224	5,0278	4,5384	6,8316	5,9794	5,2184	0.58
As (ppm)	52,1536	63,7512	1,9968	10,6161	67,2197	180,061	10.80

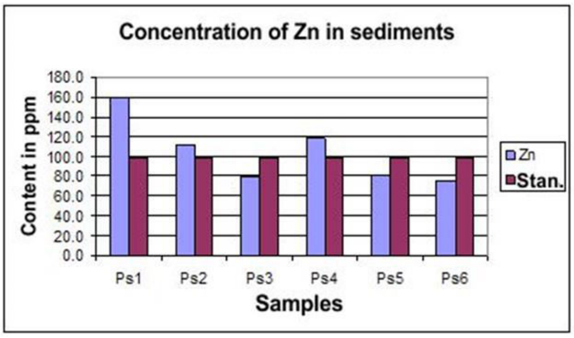


Fig. 10. Diagram of Zn concentration in samples of river sediments compared with NOAA

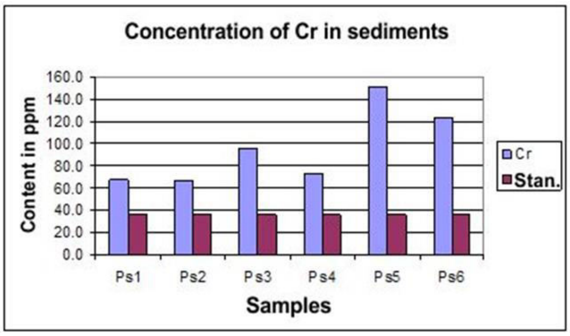


Fig. 11. Diagram of Cr concentration in samples of river sediments compared with NOAA

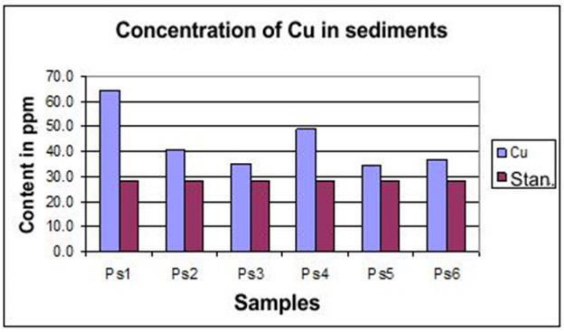


Fig. 12. Diagram of Cu concentration in samples of river sediments compared with NOAA

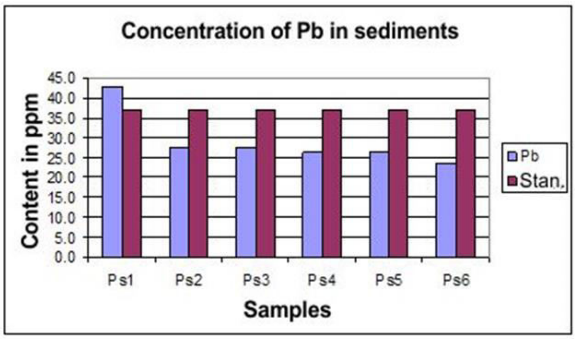


Fig. 13. Diagram of Pb concentration in samples of river sediments compared with NOAA

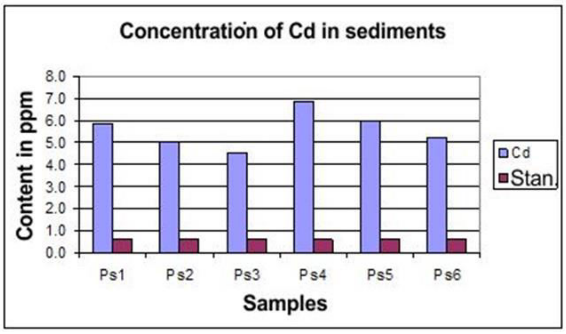


Fig. 14. Diagram of Cd concentration in samples of river sediments compared with NOAA

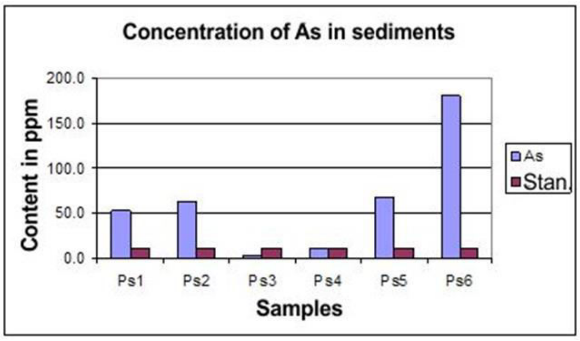


Fig. 15. Diagram of As concentration in samples of river sediments compared with NOAA

Studying the diagrams, it can be concluded that the concentration of heavy and toxic metals in the sediments is higher than that in running water.

The diagram of the zinc concentration (Fig. 10) in the sediment samples shows an increased presence. In three of the six samples there is an increased concentration related to MAC. The maximum value for Zn is registered in the Ps1 sample of 160 ppm, while the MAC is 98 ppm.

The chromium concentration (Fig. 11) in the analyzed samples is much higher than the MAC for Cr in sediments. The highest concentration is registered in the sample Ps5 151.60 ppm, and while the MAC for sediments is 36.29 ppm. There is also an increased concentration in the Ps6 sample, which is 123.27 ppm.

According to the results of the diagram for Cu (Fig. 12) it can be concluded that the concentration of copper in all sediment samples is above the MAC. Maximum values for Cu concentration were recorded in the Ps1 test of 64.46 ppm, while the NOAA standard was 28.012 ppm.

From the performed analyzes and based on the diagram for Pb concentration (Fig. 13) in the sediment samples it was determined its lower concentration in relation to the MAC, except in the sample P1 where the concentration is above the allowed limits. The MAC for Pb in sediments is 37 ppm.

According to the results obtained from the diagram for the Cd concentration (Fig. 14) in the sediment samples, its presence is visible which is higher than the MAC in all analyzed samples. In some samples the concentration is almost ten times higher than allowed. The highest concentrations of Cd is in the Ps4 test where the content of Cd is 6.83 ppm, while the MAC according to the NOAA standard is 0.58 ppm.

From the diagram for As concentration in the sediments (Fig. 15) it can be seen that in two samples there is a small concentration, below the MAC, while in the other samples it has a content above the allowed one. The MAC for As in sediment is 10.80 ppm.

5. Conclusion

From the data obtained in the tables and diagrams for water and river sediments it can be concluded that the distribution of heavy and toxic metals in the samples taken from this area is significant and in many of the analyzed samples the concentration of heavy and toxic metals is multiplied by the MAC.

In water, the distribution of heavy and toxic metals is negligible and in most of the analyzed samples their concentration is lower than the MAC, except for the concentration of As which is multiplied in almost all samples. Such concentrations of As are probably a consequence of the existence of the former Lojane Mine, i.e. its flotation tailing. The increased concentrations of heavy and toxic metals in sediments are primarily a direct consequence of the geological structure of the terrain, then the anthropogenic impacts of the former mining and tailing dumps (Lojane), treatment of arable land with organic fertilizers and physical - chemical character of aqueous solutions.

From all this stated about the distribution of heavy and toxic metals in the analyzed water and sediment samples, it follows that the reasons for their increased distribution should be sought in geology and lithology of the terrain, anthropogenic factor, primarily processing complexes and mines and organic fertilizers with which is treated arable land.

After all conclusions that emerged from the analyzes performed for the distribution of heavy and toxic metals in water and sediments, the question of their bioavailability remains open. Determining the percentage of heavy and toxic metals that participate in the food chain and is bioavailable is an open problem, the solution of which should be focused on further research.

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